Organic Compounds Associated with Hydraulic Fracturing:

Groundwater Composition and Natural Attenuation Potential

by

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Thesis submitted in partial fulfillment of
the requirements for the degree of Master of Science in the Department of
Civil and Environmental Engineering in the Graduate School
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ABSTRACT

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Abstract

As the United States slowly transitions from coal and foreign oil to more renewable energy sources, domestic natural gas is being utilized as an intermediate "bridge fuel". Advances in horizontal drilling and hydraulic fracturing have increased gas extraction and exploration over the past ten years. The massive quantities of fluids used to fracture gas-producing shale plays contain potentially toxic chemicals and the wastes are highly saline and contain naturally occurring radioactive materials. It is unclear if there are risks to shallow drinking water aquifers and if the chemical constituents of fracking fluid are inherently biodegradable if released into the environment. Monitoring the fate of these chemicals as they enter the environment is critical to understanding potential health hazards and persistence. Here, groundwater monitoring for organic compounds coupled with spatial data analysis indicates no subsurface contamination from hydraulic fracturing of the Marcellus Shale in northeastern Pennsylvania. However, a chemical fingerprint is presented suggesting increased organic compounds in shallow groundwater are due to subsurface mixing with brine containing geogenic hydrocarbons from the Marcellus Shale.

To investigate the fate and extent of the chemicals used in hydraulic fracturing and the associated wastes if released into the environment, bench-scale reactor experiments were performed. These reactors contained a synthetic hydraulic fracturing

fluid and activated sludge from a wastewater treatment plant. Bulk organic carbon decreased upwards of 76 ± 2% in a freshwater mixture and 69 ± 2% in a 10,000 mg L^{-1} NaCl saline solution. Furthermore, gasoline range organic compounds degraded over 99 ± 1% for both solutions while diesel range organic compounds recorded significantly less degradation in the saline solution than the freshwater solution (68 ± 2% and 92 ± 1%, respectively). Recalcitrant compounds of interest proved to be in the higher-molecular weight range of diesel range organic constituents. Additionally, salinity decreased the initial concentrations of both gasoline range and diesel range organic compounds in the synthetic frack solution. To explain the concentration differences in the saline reactors, the compound losses due to volatilization were quantified and further loss mechanisms were suspected to be sorption to particle surfaces.

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1. Introduction

Onshore domestic natural gas production has experienced rapid growth over the past 10 years due to advances in horizontal drilling and hydraulic fracturing in shale formations. Unconventional wells are defined as those drilled horizontally, allowing the borehole to bend 90 degrees and penetrate the target shale formation laterally up to thousands of meters [1]. Injecting a mixture of water, sand, and chemicals (collectively known as fracking fluid) at extremely high volumes (15,000 – 30,000 m^3) and under high pressures into these unconventional wells fractures the target geologic formation and releases a portion of the tightly trapped natural gas for collection at the ground surface [2]. Water and sand make up the majority of the fluid composition (around 99.5%) while the remainder is a unspecified cocktail of chemicals including acids, biocides, and surfactants [2]. Water that returns to the surface after injection is known as "flowback" water, and once natural gas is collected the returning water is called "produced" water. These wastes are often stored on site before being transported to deep well injection sites or water treatment facilities for salt and chemical removal [3].

Hydraulic fracturing is now a common practice in gas-producing shale plays around the country. Increased production has decreased natural gas prices and therefore made it one of the dominant sources of energy power generation in the U.S., at 27% of the total contribution [4, 5]. In 2012, natural gas production topped 25 trillion cubic feet, out pacing consumption increases by a factor of two [6, 7].

The Marcellus Shale formation is the largest dry gas extraction site in the United States and is estimated to contain over 140 trillion cubic feet of natural gas [8-10]. At an average of two kilometers below ground surface, it underlies 240,000 km^2 of parts of New York, Pennsylvania, Ohio, West Virginia, Maryland, Kentucky, and Virginia in the northeastern United States and is the target of thousands of both conventional oil and unconventional gas drilling operations [11-13]. Due to the recent advances in domestic natural gas exploration and extraction techniques, the Marcellus Shale in the Appalachian Basin has seen a substantial increase in hydrocarbon production in the past several years (Figure 1) [1, 14, 15].

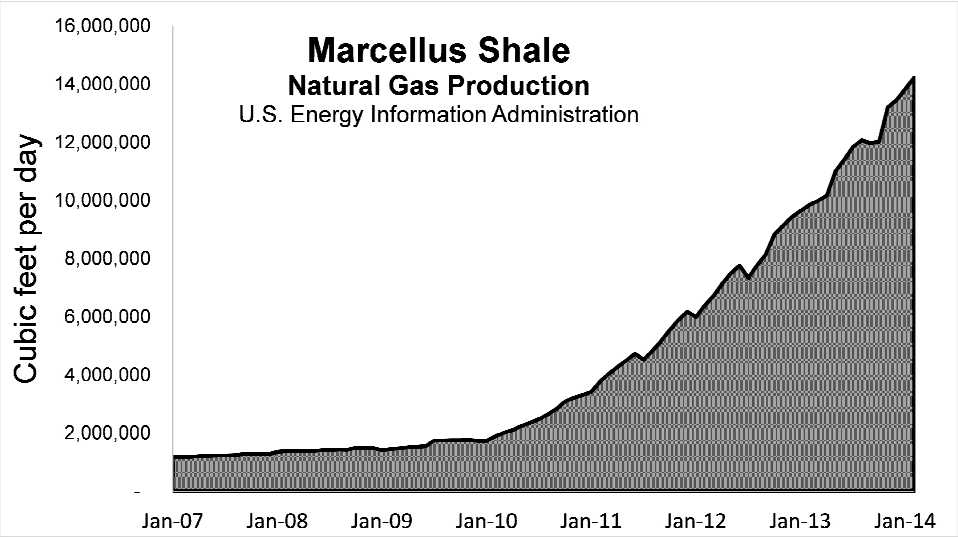

Figure 1: Substantial increase in Marcellus shale natural gas production in the past seven years. Adapted from U.S. EIA Drilling Productivity Report, January 2014 [16].

Due to the rapid growth of the industry and the novelty of the process, little is known about the environmental consequences of natural gas extraction via hydraulic fracturing. Maintaining groundwater quality is of particular concern because millions of Americans rely on private wells in rural areas where hydraulic fracturing occurs [17]. Potential connectivity of deep subsurface shale formations to shallower rock aquifers can create preferential flow paths for gasses and dissolved constituents such as natural salts, heavy metals, and organic compounds used in the fracking fluid. [18]. Recent studies in northeastern Pennsylvania have found that shallow groundwater wells within 1

km of a shale gas well contain higher average concentrations of methane than groundwater wells farther away [19, 20]. Though this data indicates an increased risk for methane contamination due to hydraulic fracturing, data with respect to dissolved organic chemicals is lacking. The EPA concluded that groundwater aquifer contamination by organic chemicals in Pavillin, WY was indeed caused by hydraulic fracturing practices in the area; however it is unclear if this contamination is unique to the particular study area or whether it is a consequence common to all unconventional drilling operations [21].

Here, I analyzed groundwater from northeastern Pennsylvania for potential hydrophobic organic chemical contamination. I also compared the groundwater organic geochemistry to inorganic chemical fingerprints for source identification. Furthermore, a collaborative degradation experiment investigated the natural attenuation potential of the fluids used in hydraulic fracturing and biodegradability of a synthetic fracking fluid is assessed to better understand how these fluids interact with the natural environment if subject to accidental release.

2. Organic Compounds in Northeastern Pennsylvania Groundwater: The Influence of the Marcellus Shale Formation and Natural Gas Extraction

In this study, I analyzed groundwater samples from private shallow drinking water wells from northeastern Pennsylvania for organic compounds to assess the impacts of hydraulic fracturing and the influence of geologic formations on groundwater chemical composition. Organic chemical analysis is of particular interest in both Marcellus Formation brine and groundwater characterization due to the concern for drinking water contamination from natural gas extraction practices. The Environmental Protection Agency (EPA) showed contamination of groundwater from organic chemicals due to hydraulic fracturing and natural gas extraction practices in Pavillion, WY, and multiple independent studies indicated the presence of methane in Pennsylvania groundwater directly linked to fracking [19-21]. Studies have explored the possibilities and risks of groundwater contamination due to migration of the chemicals in fracking fluids from target shale plays, yet no contamination from these organic chemicals has been observed in the Appalachian Basin [22-24]. This study seeks to characterize groundwater organic chemistry in northeastern Pennsylvania and identify the possible sources of organic compounds.

2.1 Hypothesis and Objectives

Compound diffusivities in tight shales (with nanodarcy permeabilities) are expected to be very low, and advective transport may be difficult to predict due to the randomness of propagating fractures and the uncertain distribution of pre-existing geologic fissures. As a result, defining "active" and "non-active" fracking zones is somewhat arbitrary. Several investigators (Osborn et al. (2011); Jackson et al. (2013)) have used a threshold of 1 km to the nearest well to define active zones in the Appalachian Basin [19, 20], and others (Fontenot et al. (2013)) have used a 3 km threshold over the Barnett Shale in Texas [25]. This evaluation of groundwater organic chemistry in northeastern Pennsylvania employs a 1 km threshold to coincide with previous studies linking methane contamination in groundwater within 1 km of a shale gas well in the same geographical region. Furthermore, unique inorganic chemical fingerprints are expected to show correlations with organic compositions due to natural influences from geologic formations (i.e., formation water equilibrated with inorganic species within the shale should also equilibrate with shale-derived organic chemicals, and these could potentially survive fluid migration to shallower groundwaters).

2.2 Experimental Design

2.2.1 Sample Collection

Shallow groundwater samples were collected in May 2012 and July 2013 from 23 and 16 homes, respectively, and one natural spring in Susquehanna and Bradford Counties in northeastern Pennsylvania (Figure 2). The wells (60 – 90 meters deep) were purged until dissolved oxygen, pH, and conductivity remained constant, at which point samples were collected. To ensure homogeneity, groundwater was collected in a precombusted 500-mL amber jar and subsequently transferred to eight 40-mL glass volatile organic analysis (VOA) vials containing 1 mL 50% v/v HCl. The sample vials were sealed with 0.125-mm PTFE-lined silicone septa and acetone-cleaned caps, then stored on ice at 4ºC until analysis.

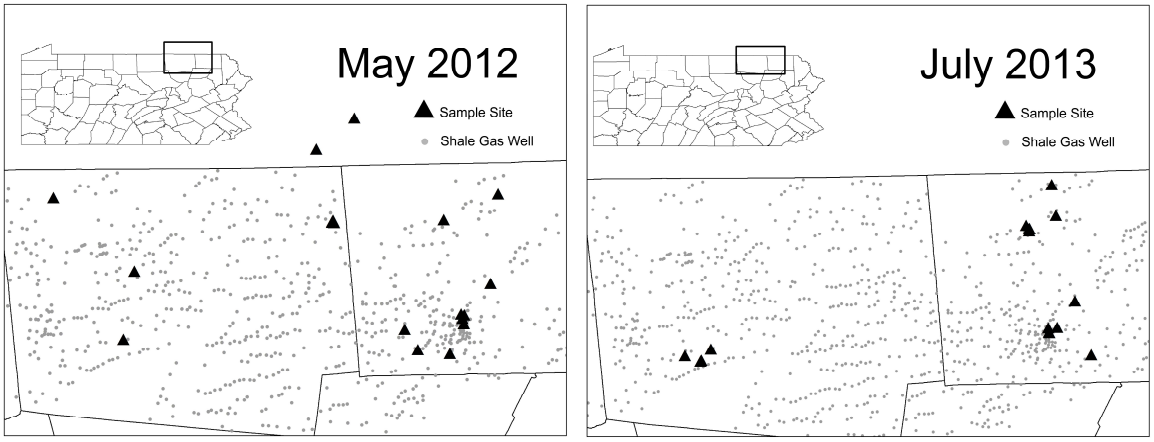

Figure 2: Groundwater sample sites relative to shale gas well locations from the May 2012 and July 2013 sampling campaigns. Note that in May 2012 two samples were collected in New York where a moratorium on fracking did and still exists.

2.2.2 Analytical Methods

Groundwater samples collected in May 2012 were analyzed for volatile organic compounds (VOCs) and gasoline range organic compounds (GRO). Samples collected in July 2013 were analyzed for VOCs, GRO, and diesel range organic compounds (DRO) by the method outlined in Appendix A.

2.2.3 Spatial Data Analysis

Spatial data for unconventional shale gas wells was obtained from the Pennsylvania Spatial Data Access and mapped with ArcGIS™. Shale gas wells were mapped along with 39 of the 40 sample locations (coordinates were not collected for one of the sample locations in Bradford County, PA). The measuring

tool was used to determine distance to nearest unconventional well, and shallow groundwater sample sites within 1 km of an unconventional shale gas well were defined as “active”, whereas those farther than 1 km from a shale gas well were defined as “non-active”.

2.2.4 Statistical Analysis

Non-parametric Wilcoxon rank-sum tests were used to statistically differentiate GRO and DRO in active and non-active frack zones, as well as geologic water types from Warner et al. (2012) [26]. Spearman correlation tests were performed on the organic compound load as related to distance to the nearest shale gas well. All statistics were run using the software program *R* and initial descriptive statistics were generated with the *UsingR* package [27, 28].

2.3 Results and Discussion

2.3.1 Groundwater Volatile Organic Compounds

The New York State Department of Environmental Conservation reported the presence of VOCs in fracturing fluid additives, including benzene, toluene, ethylbenzene, and xylenes (BTEX) in a recent environmental impact report [29]. A characterization of flowback water from both Marcellus and Barnett Shale gas

wells resulted in trace level detections of BTEX and polymethylated aromatic compounds such as 1,2,4-trimethylbenzene [30], and produced water is suspected to contain the same compounds [31, 32]. BTEX compounds are of particular interest and often analyzed in groundwater near natural gas extraction sites because of their carcinogenic properties, presence in fracking fluid and associated wastes, and regulated status [12, 33]. Due to the unknown potential of frack fluids to enter groundwater via (1) migration up from target shale plays and (2) surface spills of raw fluids and wastes, the presence of BTEX chemicals in groundwater is of interest. One model suggests that advective transport of deep subsurface fluids to groundwater aquifers could take less than 10 years due to the high volume and high pressure injection of fluids in the fracking process [34], and another study provided evidence of the migration of brines from the Marcellus Shale to shallow groundwater through natural pathways [26]. However, the migration of organic compounds from deep shales has not been established. Surface spills could also threaten VOC contamination in groundwater. One study analyzed data from 77 surface spills related to hydraulic fracturing operations in Colorado and found BTEX concentrations in excess of national drinking water standards [35].

Of the 40 shallow groundwater samples, only six contained trace amounts of target analytes. Target analytes (see Appendix C) included halogenated VOCs and BTEX compounds; BTEX were the primary constituents present above detection limits (Table 1).

Table 1: Detected VOCs in shallow groundwater relative to EPA maximum contaminant levels. Detection limits are outlined in Appendix C.

Compound	MCL[a] ng mL^{-1}	PAS310[b] ng mL^{-1}	PAS311[b] ng mL^{-1}	PAS312[b] ng mL^{-1}	DPA351[b] ng mL^{-1}	PAW241[c] ng mL^{-1}	PAB298[c] ng mL^{-1}
Benzene	5	ND[d]	ND	0.153	ND	ND	ND
Toluene	10^3	0.702	0.597	0.185	0.640	0.14	0.260
Ethylbenzene	700	0.074	ND	ND	ND	ND	ND
Xylenes (total)	10^4	0.201	ND	0.200	0.894	ND	ND

Note: [a] Maximum contaminant level; [b] July 2013 sample; [c]May 2012 sample; [d] Not detected

All detected VOCs were orders of magnitude below EPA maximum contaminant levels (MCL). The MCL for benzene in drinking water is the most strict of all BTEX compounds at 5 ng mL^{-1}, and it was detected in only one of the 40 samples at a slight fraction of the recommended limit (0.15 ± 0.11 ng mL^{-1}; LOD: 0.20 ng mL^{-1}). This concentration is exceptionally low. In contrast, Gross et al. (2013)

reported the mean concentration of benzene measured in groundwater from the 77 surface spills in Colorado at 1400 ng mL^{-1} [35]. Although too few samples contained VOCs above the detection limits to generate spatial data statistics, the extremely low levels of BTEX is a strong indicator that the sampled northeastern Pennsylvania groundwater is not contaminated with VOCs, and their presence is most likely not related to hydraulic fracturing activity.

2.3.2 Groundwater Gasoline Range Organic Compounds

Gasoline range organic compound analysis allows environmental chemists to see a general scope of lower molecular weight hydrocarbons in a system without having to identify each compound. Ten of the 40 samples analyzed in this study contained gasoline range organic compounds above the detection limit (LOD: 0.03 ppb; Figure 3). Concentrations were as high as 8.80 ± 0.48 ppb, and 30 of the samples had no detectable GRO.

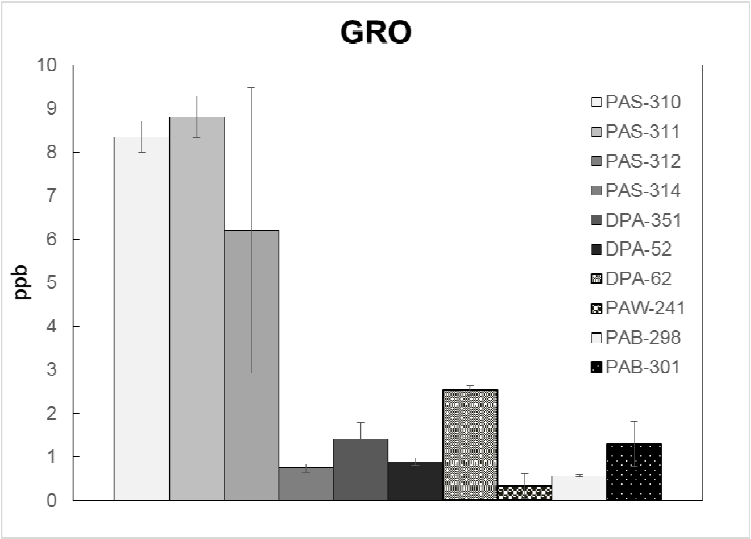

Figure 3: Samples containing detectable gasoline range organic compounds out of the 40 collected in the May 2012 and July 2013 sampling campaigns. Samples PAS-310 through DPA-351 were from July 2013, and samples DPA-52 through PAB-301 were from May 2012. Sample labels are arbitrary to protect homeowner identities.

Although a thorough record of northeastern Pennsylvania groundwater organic compounds is not available, the low levels suggest that the detected GRO is from the natural background. By contrast, an EPA study of contaminated groundwater near Pavillion, WY detected GRO as high as 3710 ppb in a monitoring well, and the source was speculated to be from hydraulic fracturing [21]. The levels detected in this study and the concentrations found in northeastern Pennsylvania groundwater are vastly different, but based on

concentrations alone, we cannot conclude that 8.80 ppb GRO is caused by natural gas extraction practices nor due to natural geologic influences.

Spatial analysis of GRO indicated no influence from hydraulic fracturing in the sample region. Groundwater samples were collected from homes as close as 0.12 km to a shale gas well and as far away as 14.2 km. GRO from sample locations within 1 km of an unconventional shale gas well (active) and farther than 1 km (non-active) were not significantly different (i.e., a Wilcoxon non-parametric rank-sum analysis indicated no significant difference ($p = 0.60$) in GRO concentrations based on active or non-active zones (Figure 4)).

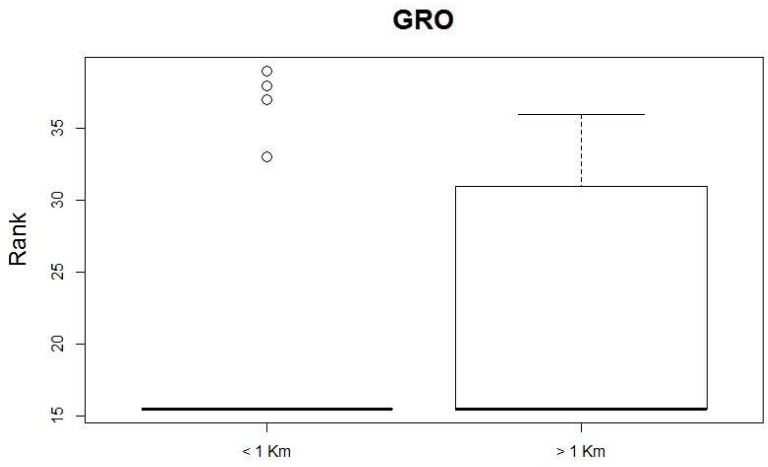

Figure 4: Ranked gasoline range organic compounds in shallow groundwater from active and non-active gas extraction zones. Wilcoxon rank-sum tests proved no significant difference ($p = 0.60$; $n = 22$ in < 1 km group; $n = 17$ in > 1 km group).

GRO concentrations and distance to the nearest shale gas well showed no statistically significant correlation (Figure 5; non-parametric Spearman rank correlation analysis indicated no significant correlation between a shallow groundwater sample location and its distance to the nearest unconventional shale gas well ($\rho = 0.19$, $p = 0.24$)).

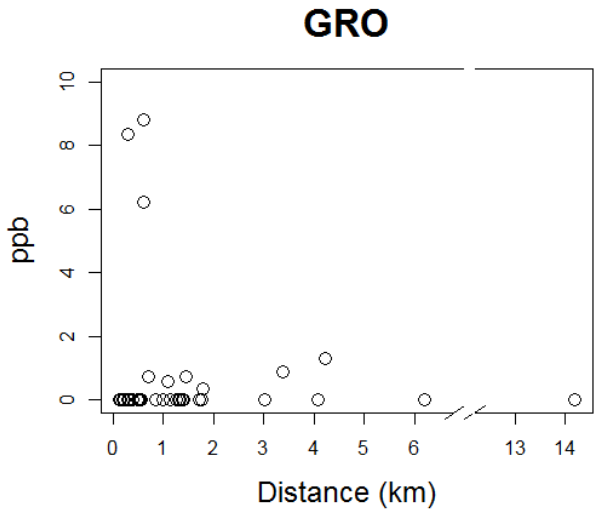

Figure 5: Gasoline range organic compounds in shallow groundwater with respect to distance to the nearest shale gas well. Spearman rank correlation analysis was insignificant ($\rho = 0.19$, $p = 0.24$; n= 39).

If there was contamination due to hydraulic fracturing, the expected plot would display increased organic compound concentrations as distance to the nearest well decreased, and the Spearman ρ would approach -1. The calculated ρ of 0.19 indicates a weak positive correlation, however $p = 0.24$ indicates that the ρ value is not significantly different from zero (no correlation). The statistically insignificant correlation and lack of significance between active and non-active frack zones suggests that natural gas extraction is not the source of gasoline range organic compounds in the shallow groundwater samples analyzed.

The EPA does not have a recommended MCL for gasoline range organic compounds, as it is a cumulative index of many volatile organic compounds; however, the U.S. Department of Health and Human Services sets a recommended maximum level for total petroleum hydrocarbons (TPH) in drinking water at 200 ppb [36]. GRO is a small fraction of TPH, and the concentrations detected are of little concern at such low levels. The homeowners of the sample locations should not be alarmed at the presence of GRO and no action is required to remove it from their drinking water.

2.3.3 Groundwater Diesel Range Organic Compounds

Higher molecular weight semi-volatile compounds are included in the DRO analysis. All 17 samples extracted by liquid-liquid extraction (LLE) contained detectable amounts of diesel range organic compounds (LOD: 0.09 ng mL $^{-1}$; Figure 6). Concentrations ranged from 0.74 ± 0.01 to 158 ± 3 ng mL^{-1}.

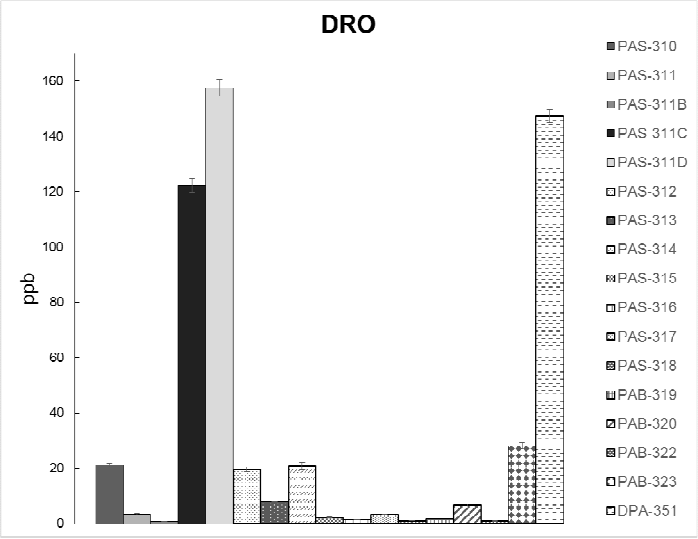

Figure 6: Diesel range organic compounds detected in the July 2013 samples collected in Susquehanna and Bradford Counties, Pennsylvania. All 17 samples had diesel range organics.

The range of concentrations is much greater than that of GRO and the most abundant concentration seems relatively high. However, the EPA reported DRO concentrations in their contaminated Pavillion, WY monitoring well as high as 4050 ppb and attributed this detection to the solvents, surfactants, and breakers

used in the fracking process [21]. Those concentrations are significantly greater than any DRO concentrations detected in the northeastern Pennsylvania field site for this study.

Limited data is available on natural background DRO levels in northeastern Pennsylvania; however, some states such as Minnesota report that groundwater aquifers are defined as contaminated with petroleum compounds when concentrations exceed 1000 ppb [37]. The detected DRO in northeastern Pennsylvania are far below contamination thresholds, and therefore cannot be tied directly to natural gas extraction practices by virtue of concentration alone.

Spatial analysis of DRO also produced insignificant relationships between active and non-active zones and overall distance from shale gas wells. DRO concentrations in active fracking zones (< 1 km) were more variable and had a broader distribution than those in non-active zones; however, the Wilcoxon rank-sum test was insignificant ($p = 1.0$) in determining a statistical difference between zones (Figure 7). In other words, there was no significant difference in the mean DRO concentrations within and outside of 1 km from a well pad.

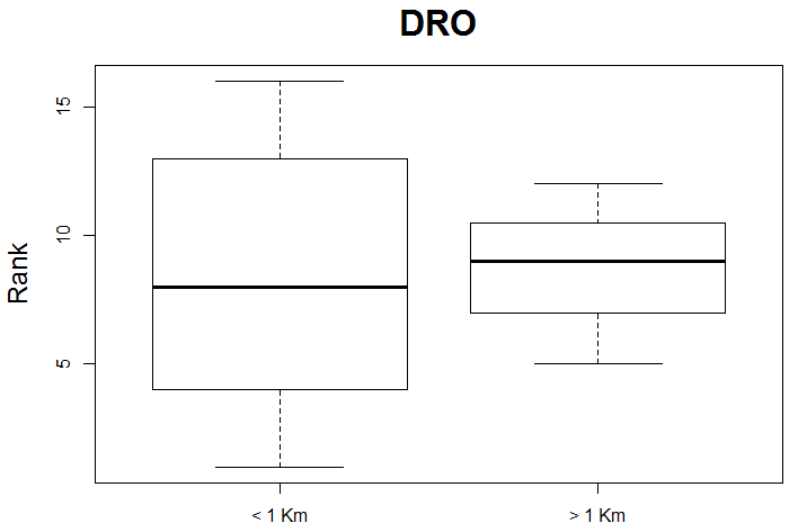

Figure 7: Ranked diesel range organic compounds in shallow groundwater from active and non-active gas extraction zones. Wilcoxon rank-sum tests proved no significant difference ($p = 1.0$; $n = 13$ in < 1 km group; $n = 4$ in > 1 km group).

The spatial correlation of DRO was very similar to GRO although on a much smaller distance scale. Between the May 2012 and July 2013 sampling campaigns, a large number of shale gas wells were drilled and in production (Figure 2). Sampling locations were chosen based on their proximity to new shale gas wells. Because of this, the farthest distance away from a gas well was only 1.5 km (Figure 8). A Spearman rank correlation indicated no significant correlation between DRO concentrations in shallow groundwater and the sample proximity to a shale gas well ($\rho = -0.01$, $p = 0.96$).

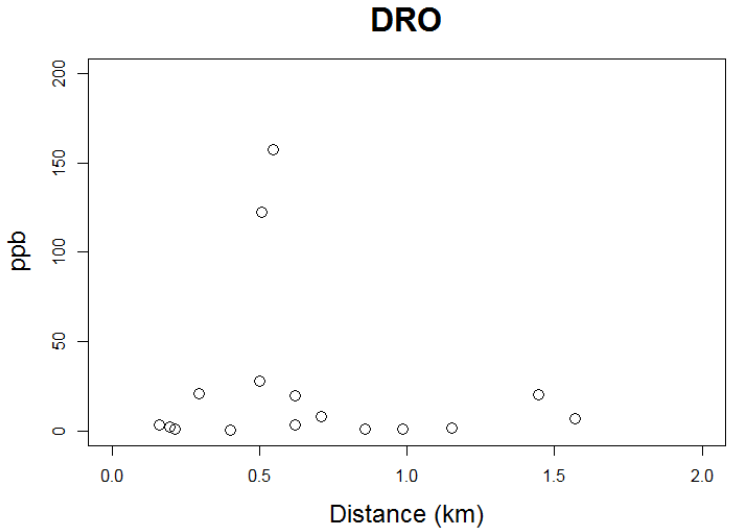

Figure 8: Diesel range organic compounds in shallow groundwater with respect to distance to the nearest shale gas well. Spearman rank correlation analysis was insignificant ($\rho = -0.01$, $p = 0.96$; $n = 16$). Note, the farthest sample location from a shale gas well was 1.57 km.

DRO concentrations tended to increase slightly as distance from a shale gas well decreaseed. This is supported statistically by a negative Spearman ρ value. However, the weak ρ (-0.01) and high p-value (0.96) indicate that this conclusion is invalid and the correlation is not statistically different from zero. Without DRO analysis of actual hydraulic fracturing fluid, the insignificant chemical and spatial data relationships cannot prove whether or not fracking is the actual source of the organic compounds.

Similarly to GRO, maximum contaminant levels do not exist for DRO as specified by the EPA. DRO is also a fraction of TPH and therefore should not be a cause for concern to homeowners because all concentrations were less than the recommend maximum level for TPH at 200 ppb [36].

2.3.4 Geologic Implications

2.3.4.1 Groundwater Classification

To further investigate the possible source of these organic compounds, comparisons with inorganic chemical analyses were explored. Warner et al. (2012) characterized shallow drinking water aquifers in the Appalachian Basin and provided evidence that some groundwater salinization results from the migration of Marcellus Formation brine through naturally occurring pathways [26]. Four shallow groundwater classifications were developed based on salinity, molar ratios of Na/Cl and Br/Cl (Table 2.)

Table 2: Shallow drinking water aquifer classification by inorganic geochemical characteristics. Adapted from Warner et al. (2012).

Water Type	Salinity (Cl, mg/L)	Na/Cl	Br/Cl	Other
A	< 20	> 5	> 0.001	$CaCHO_3$
B	< 20	> 5	> 0.001	$NaCHO_3$
C	> 20		< 0.001	NO_3^-
D	> 20	< 5	> 0.001	

Additionally, isotopic Sr^{87}/Sr^{86} ratios suggested another inorganic chemical fingerprint of Marcellus Formation brine [38]. Linear correlations between Sr and Cl, and decreasing Sr^{87}/Sr^{86} with increasing Sr concentrations, further suggested that Type D classified groundwater salinization is a result of Marcellus Formation brine mixing [26]. The water-typing classification from Warner et al. (2012) was used throughout this study to compare the organic geochemistry of groundwater collected in northeastern Pennsylvania.

The 40 groundwater samples collected in May 2012 and July 2013 for organic compound analyses were also analyzed for inorganic compounds and categorized into water types. Fifteen samples were Type A, 5 were Type B, 8 were indistinguishable between Type A and B, and 12 contained Marcellus-like characteristics and were classified as Type D. These water types were condensed into two groups for statistical comparisons and used to determine whether or not total organic compounds were reflective of geologic influence. Those that included inorganic chemical characteristics of Marcellus Shale brine were defined as Type D, and those that did not (Types A, A/B, and B) were grouped into together as Type A/B.

2.3.4.2 Organic Compounds and Water Type

Gasoline range organic compounds were ranked between water types for statistical analysis. Type D water contained greater concentrations of GRO than did Type A/B (Figure 9), where Type D water average GRO concentration was 1.11 ± 0.82 ppb compared to 0.54 ± 3.28 ppb for Type A/B. The ranked differences are statistically significant from one another (p = 0.004, Wilcoxon rank-sum test).

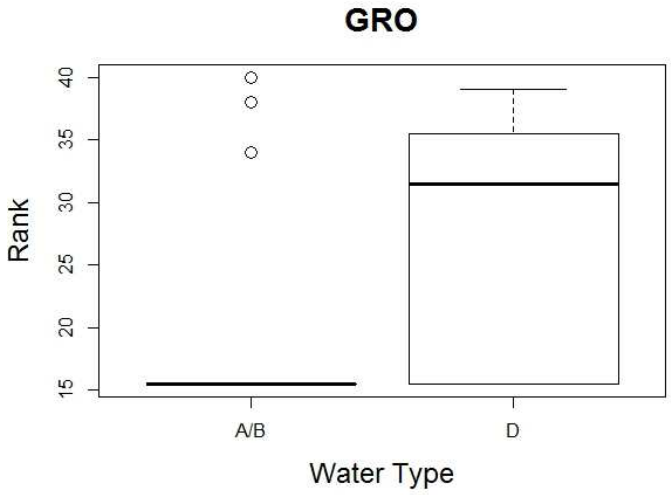

Figure 9: Ranked gasoline range organic compounds between water types. Statistically significant differences (p = 0.004, Wilcoxon rank-sum test) suggest shallow groundwater with Marcellus Formation inorganic chemical characteristics contain more GRO than groundwater with meteoric influence.

Gasoline range organic compounds are essentially a cumulative range of volatile organic compounds including low boiling point compounds. The abundance of

natural gas and the nature of the organic-rich shale play suggest that volatile organic compounds could be released along with the brine and migrate upward through natural pathways, contributing to GRO in groundwater.

Diesel range organic compounds displayed a similar result (Figure 10). Twelve shallow groundwater samples were classified as Type A/B, and 5 were Type D. Type D water contained significantly more DRO on average (42.24 ± 0.90 ppb) than Type A/B (27.86 ± 4.24 ppb) ($p = 0.08$, Wilcoxon rank-sum test).

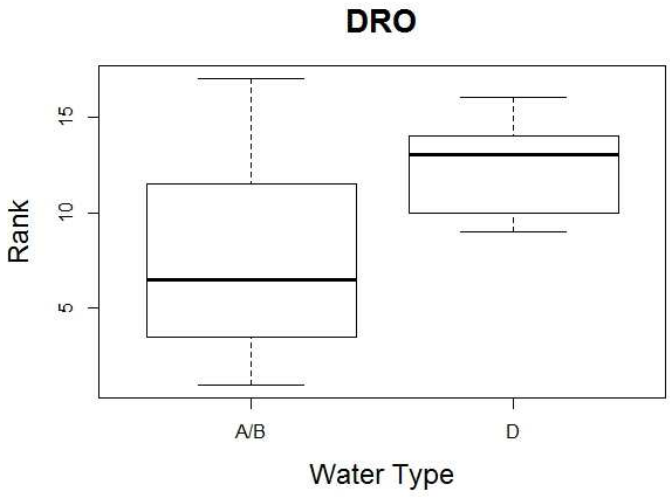

Figure 10: Ranked diesel range organic compounds between water types. Moderate statistical significance ($p = 0.08$) suggests shallow groundwater with Marcellus Formation characteristics contain more DRO than groundwater with meteoric influence.

A true geogenic organic chemical analysis of Marcellus Formation brine is difficult due to anthropogenic chemical backgrounds such as drilling additives and fracking fluid. However, algal deposits that created the sedimentary shale play would contribute to aliphatic hydrocarbons [39, 40]. These compounds could migrate along with brine through natural pathways and elevate DRO concentrations in Type D water.

The sample locations in Northeastern Pennsylvania were primarily in rural agricultural environments. Leaching of chemicals from agricultural practices can contaminate groundwater. Agricultural practices are a proven source of groundwater contamination with organic pesticides, herbicides, and inorganic compounds such as nitrate and phosphate [41, 42]. Pesticides are semi-volatile organic compounds which would contribute to overall DRO concentrations, thereby adding a positive bias and skewing the data. Groundwater nitrate concentrations are an important field parameter in determining pesticide contamination and could provide an indication of the extent of GRO and DRO leaching [43]. Eleven of the 17 samples collected in July 2013 and analyzed for GRO and DRO were also analyzed for nitrate by Duke University researchers, and all contained detectable quantities. Spearman rank

correlation tests showed no significance between GRO and nitrate ($\rho = 0.40$, $p = 0.22$) nor DRO and nitrate ($\rho = 0.35$, $p = 0.29$). Although the tests are from a small subset of the total sample population, the results suggest no influence of leaching from agricultural practices on groundwater organic compounds when using nitrate as an indicator and further supports the conclusion that the chemicals are influenced by mixing with Marcellus shale brine.

2.4 Conclusions and Future Research

Organic compound analysis of shallow groundwater from private residential wells in areas of hydraulic fracturing show a chemical influence from natural geologic formations and not natural gas extraction practices. Low concentrations of volatile organic compounds were detected in only a small subset of groundwater samples. This, along with the lack of correlation between gasoline or diesel range organic compounds and distance to the nearest shale gas well, suggest that hydraulic fracturing is not affecting organic compounds present in the groundwater. Instead, the origin of the groundwater and the Marcellus Formation brine are the source of elevated levels of gasoline and diesel range organic compounds. This study is not the first to conclude that hydraulic

fracturing is not contaminating northeastern Pennsylvania groundwater with organic chemicals [44, 45]. It is, however, the first to present data indicating that shallow groundwater organic geochemistry in northeastern Pennsylvania can be impacted by the Marcellus Shale Formation. Warner et al. (2012) suggest that areas with Type D water could have a higher risk of contamination from hydraulic fracturing due to enhanced hydraulic conductivity in the geologic formations that assist the migration of subsurface brines [26]. With the organic geochemical evaluation and conclusions from this study, the petroleum industry could benefit by performing quick analyses of GRO and DRO in groundwater at potential gas extraction sites. Low or undetectable concentrations of organic compounds in shallow groundwater could provide an indicator for gas extraction zones that have a lower potential risk for possible upward migration of fluids from the deep subsurface.

As DRO was found in each shallow groundwater sample, a specific analysis of individual compounds may provide insight to particular compounds that are representative of the Marcellus Formation. Further research in this area will include a targeted analysis of higher molecular weight semi-volatile organic compounds and seek to quantify a specific organic geochemical fingerprint of

groundwater with natural mixing of Marcellus Formation brine. Continued monitoring of organic compounds in groundwater from northeastern Pennsylvania will also provide information of the natural environmental background, which will be useful in future analyses of the effects of hydraulic fracturing.

3. Natural Attenuation of Hydraulic Fracturing Fluid

In early 2008, more than 4.5 million liters of hydraulic fracturing fluid were released on the Roan Plateau, Colorado and ultimately into tributaries of the Colorado River by an accidental spill at a shale gas extraction site [46]. In 2009, over 30,000 liters of fracking fluid were spilled at a site in Dimock, Pennsylvania, contaminating a nearby creek with potentially toxic chemicals causing fish kills [47]. These spills are just two examples of the realities that accompany natural gas extraction practices. Little research has focused on the potential for the natural attenuation of fluids associated with hydraulic fracturing when released into the environment. Accidental release of hydraulic fracturing fluids and produced waste is a major concern due to the substantial volumes (15,000 – 30,000 m^3) used in gas extraction and the potential for operator

handling errors. The environmental fate and inherent biodegradability of these fluids is largely unknown and is the focus of an ongoing collaboration between The Plata Lab at Duke University and The Mouser Lab at The Ohio State University.

Preliminary studies of synthetic hydraulic fracturing fluid degradation, conducted at The Ohio State University, indicate that a substantial portion (approximately 25%) of organic compounds used in fracking fluids are recalcitrant to microbial degradation as measured by dissolved organic carbon (DOC) (Figure 11). The chemical composition of the remaining 25% is largely unknown.

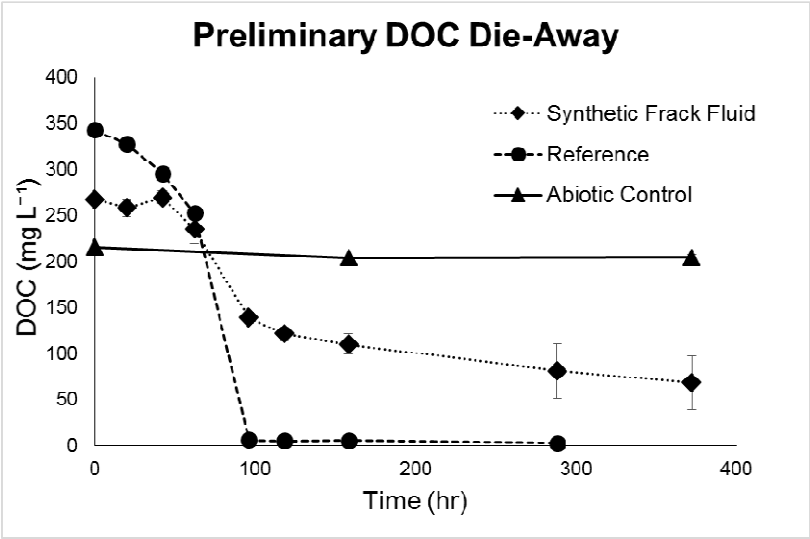

Figure 11: Preliminary biodegradation results of DOC die-away with activated sludge in aerobic freshwater conditions. Synthetic fracking fluid (measured as DOC) degraded 75.0 ± 0.1 % after 53 days. The reference solution contained acetate and activated sludge. Results were recorded by The Mouser Lab at The Ohio State University.

This study seeks to identify persistent compounds over a range of typical environmental conditions found in fracking fluids and wastes, as measured in a synthetic fracking fluid. It also attempts to quantify the rate and extent of biodegradation potential in both natural and engineered environments. With this information, the natural gas industry will be better informed of the environmental persistence of the fluid and waste with the hope that local and

state agencies can better prepare remediation strategies in the event of an accidental release.

3.1 Hypothesis and Objectives

Extremely high salinities (total dissolved solids (TDS) > 100,000 mg L^{-1}) exist in shale formation brines due to seawater evaporation over geologic timescales [48]. Produced and flowback water from shale gas wells not only contain the high TDS brine, but also the chemicals used in the drilling and fracking process [30-32]. Comparing the rate and extent of fracking fluid degradation by aerobic microorganisms under a range of salinity conditions can simulate surface-spill natural attenuation and treatment at municipal waste water treatment plants (MWWTP). Increased salinity is expected to inhibit the rate and magnitude of degradation by aerobic microbes found in MWWTPs and cause certain organic compounds to persist over time. We expected alkylated and halogenated aromatic hydrocarbons to be persistent and lower molecular weight and straight-chain hydrocarbons to be preferentially degraded in the experimental reactors.

3.2 Experimental Design

3.2.1 Synthetic Fracking Fluid Preparation

The Mouser lab at The Ohio State University prepared a synthetic mixture of hydraulic fracturing fluid following the FracFocus Chemical Disclosure Registry [49, Table 3]. Oil and gas companies are not required to report the chemical mixtures used in their operations, however those that do have provided a general guideline for the constituents in fracking fluid. The synthetic fluid used in these experiments is a general mixture based on reported chemicals from extraction wells in the Marcellus Shale. Water and sand make up approximately 99% of the total mass of the synthetic fluid, while the rest is comprised of corrosion inhibitors, surfactants, biocides, and water gelling agents (Table 3). This synthetic frack fluid is the target substrate for microbial degradation experiments. Experimental reactors (Erlenmeyer flasks) were adjusted to pH 7.4 ± 0.2 with 1 M NaOH and covered with aluminum foil (intentionally aerobic and open to the atmosphere) while continuously shaken in the dark at 22 °C. Samples for organic compound analyses were collected in volatile organic analysis (VOA) vials with 1 mL 50% v/v HCl and sealed with acetone cleaned caps and PTFE-lined silicone septa before shipping on ice to Duke University.

Table 3: Synthetic fracking fluid components and respective application in high volume hydraulic fracturing.

Additive	Use	Percent Mass
Water		84.7
Sand	proppant	14.6
Hydrochloric Acid	mineral dissolution	0.35
Citric Acid	precipitant inhibitor	0.0025
AI – 600[a]	corrosion inhibitor	0.0009
Revert Flow[a]	surfactant	0.057
CC – 120[a]	clay stabilizer	0.091
WGA 15L[a]	water gelling agent	0.11
Nalco EC6110A[a]	biocide	0.023
Ethylene glycol	fluid stabilizer	0.0082
Boric acid	viscosifier	0.0082
Ethanolamine	viscosifier	0.0082
Sodium Chloride	clay stabilizer	0.0008
Potassium Carobonate	pH adjustor	0.0006
Potassium Hydroxide	pH adjustor	0.0006

[a] Trade name

3.2.2 Bulk Carbon Degradation

DOC was used as the preliminary measure of bulk frack fluid degradation. The method followed the Organization for Economic Co-operation and Development (OECD) Method 301A for DOC die-away to understand the extent and kinetics of bulk degradation [50]. A starting seed of 25 mg L^{-1} activated sludge from a MWWTP (Alum Creek Water Reclamation Facility, Lewis Center, OH) was added to the mixed and aerated flasks containing the

synthetic frack fluid and varying levels of salinity (TDS as NaCl). The starting substrate DOC (synthetic frack fluid) was around 200 mg L^{-1}. Total dissolved solids concentrations were 0, 10,000, and 60,000 mg L^{-1} as NaCl. Bulk DOC was measured with a TOC-V CSN Total Organic Carbon Analyzer (Shimadzu Corp.) equipped with a 720 °C combustion chamber over the course of 270 hours and percent degradation were calculated based on measured starting concentrations. All DOC measurements were performed at The Mouser lab at The Ohio State University before collection for specific organic chemical analysis.

3.2.3 Organic Chemical Analysis

To provide an in-depth profile of biodegradation, a more detailed organic chemical analysis was performed. Individual targeted VOCs, GRO compounds, and DRO compounds were measured and quantified by the method outlined in Appendix A. GRO and DRO compounds quantified the extent of degradation over lower boiling point and higher boiling point nonpolar compounds that can be analyzed by gas chromatography (GC). The VOC analysis provided insight to low molecular weight recalcitrant compounds not readily degraded in an environmental scenario. Raw samples of the synthetic frack fluid were analyzed

but not included in the report due to analytical challenges with both purge and trap GC analysis and LLE sample preparation.

3.3 Results and Discussion

3.2.1 Bulk Carbon Degradation

DOC was measured at nine time points over the course of 270 hours for solutions containing the synthetic frack fluid with 0, 10,000, and 60,000 mg L^{-1} TDS as NaCl. Starting concentrations were slightly less than 200 mg L^{-1} DOC for each sample, and reductions were recorded in all but the 60,000 mg L^{-1} TDS sample (Figure 12). The samples were defined as Freshwater, Mid salinity, and High salinity to correspond with 0, 10,000, and 60,000 mg L^{-1} NaCl, respectively.

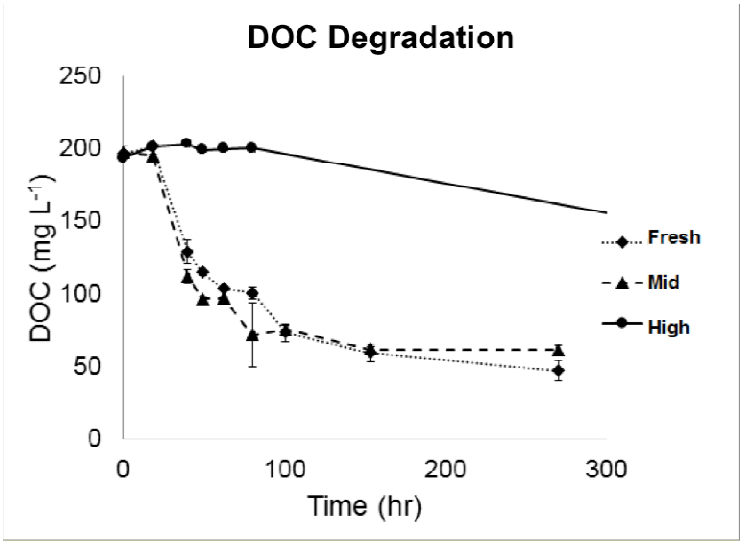

Figure 12: Bulk carbon degradation in synthetic frack fluid of varying salinities. Fresh, Mid, and High labels correspond to salinities (0, 10,000, and 60,000 mg L^{-1}, respectively). Note the small decrease in DOC of the High sample, which had 57% degradation after 654 hours (point not shown). Results courtesy of The Mouser Lab at The Ohio State University.

A 76 ± 2% reduction in DOC was measured in the Freshwater sample and the Mid salinity sample recorded a 69 ± 2% reduction.

Rate constants and half-lives were calculated with first order rate kinetics simulating a treatment system with cell recycle or environmental attenuation on the ground surface. DOC concentrations were natural-log transformed in order to achieve normality for regressions. A linear least squares regression was generated in *R* for the model by Equation 1.

$$lnC_t = -kt + lnC_0 \qquad \text{Equation 1}$$

The calculated slope and intercept (k and C_0) obtained from the model were then used to calculate and plot first order decay curves by Equation 2 (Figure 13).

$$C_t = C_0 e^{-kt} \qquad \text{Equation 2}$$

Decay rates for the Fresh and Mid salinity samples were both significant ($p < 0.05$) and calculated as 0.13 d^{-1} and 0.10 d^{-1}, respectively.

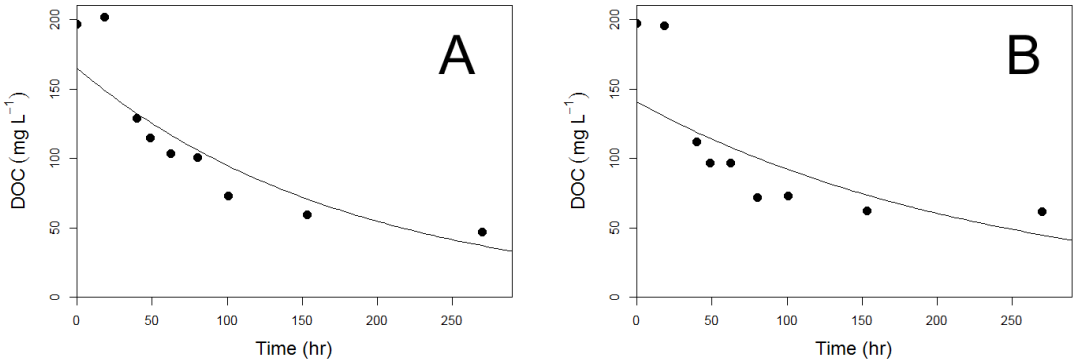

Figure 13: Bulk dissolved organic carbon observed decay in a Freshwater (A) and Mid salinity (B) reactor plotted with a least squares regression based on a natural-log transformed linear model (A: $r^2 = 0.85$, $p < 0.05$; B: $r^2 = 0.61$, $p < 0.05$)

Both regressions and decay constants were statistically different from zero ($p < 0.05$); however, they are not statistically different from one another ($p = 0.61$, Student two-tail test). This indicates that salinity of at least 10,000 mg L^{-1} as NaCl does not affect the microbial degradation of synthetic fracking fluid.

The decay model obtained from the linear fit of the High salinity sample (60,000 mg L^{-1}) proved to be different than the Fresh and Mid models. The regression for the High sample model was strong ($r^2 = 0.98$, $p < 0.05$) and the decay constant was less than the other models ($k = 0.02\ d^{-1}$, $p < 0.05$) as expected due to the little microbial degradation as seen in Figure 12. Individual comparisons of the calculated regression of the High sample with both Fresh and Mid regressions indicated a strong significant difference ($p < 0.001$, Student two-tailed test). These results suggest that the high salinities commonly found in hydraulic fracturing wastes can significantly inhibit microbial degradation of bulk dissolved organic carbon. This claim is further supported by studies that detail microbial degradation inhibition in wastewater treatment due to highly saline water [51, 52]. Water exhibiting hypersaline properties can even be recalcitrant to biological treatment [53], and could potentially explain the lack of DOC degradation in the High salinity frack fluid sample.

Although typical activated sludge MWWTP processes can contain mixed-liquor suspended solids concentrations up to 5,000 mg L^{-1} and have solids retention times of up to 14 days [54], the results of this study suggest that treatment facilities may be inadequate in organic compound removal due to the

necessary retention times for sufficient removal (55 days for 95% DOC removal in the High salinity frack fluid based on 0.02 d^{-1} decay rate). Complete removal of the synthetic fracking fluid compounds was not possible. Approximately 25% of the DOC remained in the Freshwater solution after 270 hours. Therefore, this fraction may be a concern to overall microbial degradation in natural or conventional engineered treatment systems. Furthermore, natural environmental conditions are unlike the ideal laboratory conditions present in this experiment. A spill of frack fluid or wastewater on the ground surface or into a stream would not be consistently aerated and mixed with activated sludge, and therefore could exhibit much longer DOC half-lives in natural systems. The recalcitrant compounds comprising the remaining 25% needs to be thoroughly investigated to further understand which chemicals in particular are used in hydraulic fracturing fluid and are resistant to microbial degradation.

3.2.2 Gasoline Range Organic Compounds

Four samples from each time point (2 Fresh samples, 2 Mid salinity samples) were analyzed at 18.5, 49, and 270 hours after the start of the experiment for gasoline range organic compounds. Only three time points were chosen for organic chemical analysis due to the small amount of sample

remaining in the experimental reactors. The High salinity samples (60,000 mg L^{-1} TDS) were not analyzed because of the lack of DOC degradation measured before GRO sample preparation. Nearly all of the GRO compounds were degraded in each of the four samples (Figure 14). GRO was reduced by 99 ± 1% in the freshwater samples and 99 ± 0.2 % in the low salinity samples. These results indicate that lower boiling point organic compounds have a high potential for biodegradation in freshwater and saline solutions.

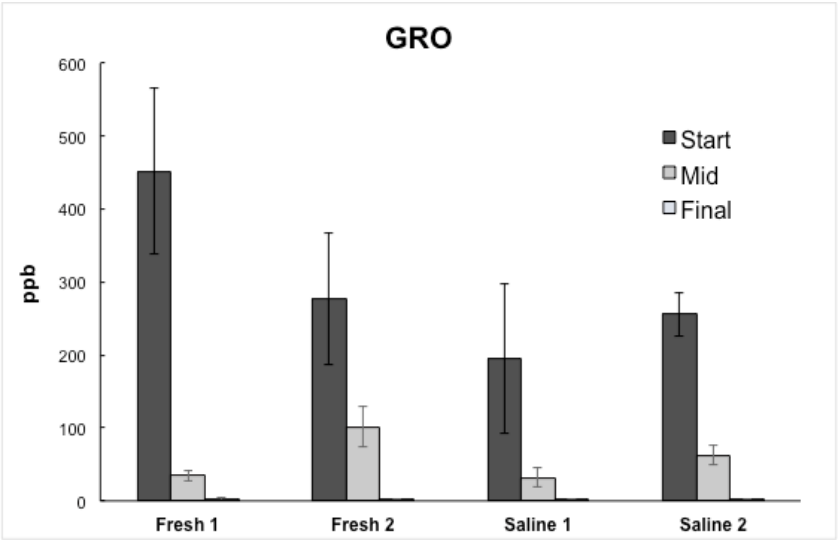

Figure 14: Gasoline range organic compound degradation in synthetic frack fluid after three time points when spiked with 25 mg L^{-1} activated sludge. The freshwater samples contain no salt and the saline samples contain 10,000 mg L^{-1} NaCl. Start = 18.5 h, Mid = 49 h, Final = 270 h.

All four samples had final GRO concentrations between 1.30 and 2.54 ppb; however, their starting concentrations and standard deviations varied greatly. During the 4 minute purge at the start of the instrumental analysis the samples began to bubble and create a foam that rose in the purge and trap sparger. The foaming nature of the samples is most likely caused by the presence of surfactants in the frack fluid. Some samples foamed more than others, potentially due to a lack of homogeneity in the sample vials, and could be the cause of the increased variability observed in the first time points. Nevertheless, it is evident that GRO compounds are susceptible to biodegradation under these experimental conditions. These results are supported by previous studies reporting high removal of VOCs in MWWTPs [55] and indicate that gasoline range organic compounds would behave similarly in batch reactors with activated sludge.

Abiotic controls to account for loss through volatilization were not analyzed via GC in this experiment. Further, the raw synthetic frack fluid presented an analytical challenge that prevented an accurate measurement of GRO compounds without degradation. The foaming of the surfactants during the purge step precluded a complete analysis.

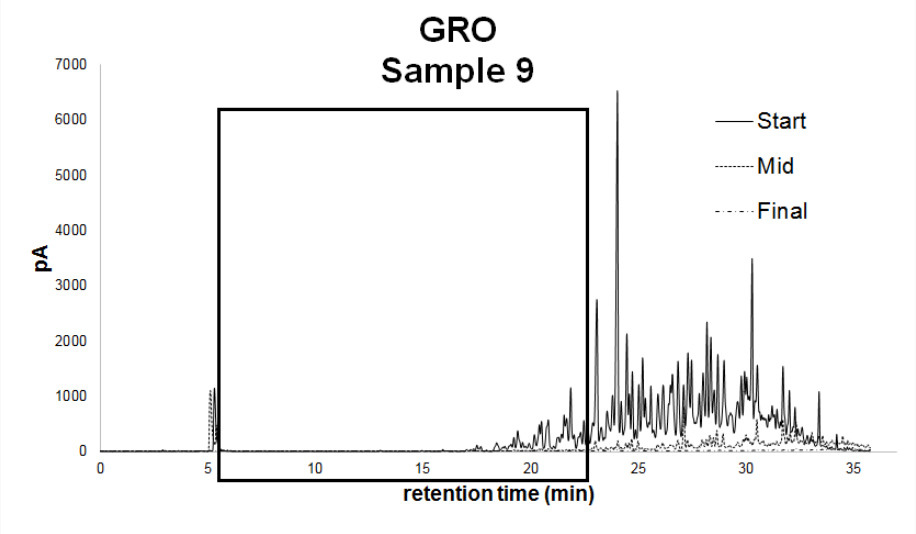

Figure 15: Overlaid chromatograms of a freshwater sample degradation analyzed by purge and trap GC-FID for gasoline range organic compounds. The black box indicates the retention time range for GRO (3-methylpentane to 1,2,4-trimethylbenzene). Note the unresolved complex mixture (UCM) and the extent to which it is included in the GRO analysis.

An unresolved complex mixture (UCM) was present in the chromatogram and is indicative of unresolved hydrocarbons. Although not targeted in GRO analysis (see Figure 15), a potential source of the UCM is the petroleum distillate additives used in the frack fluid as the water gelling agent, WGA 15L. Future experiments to qualitatively analyze the raw synthetic frack fluid will include

acid-base partitioning and petroleum fractionation column chromatography to separate aliphatic and aromatic hydrocarbons.

To quantify the UCM as seen in Figure 15, an "extended GRO" value was calculated. Instead of the total cumulative area between 3-methylpentane (retention time ~ 5.4 min.) and 1,2,4-trimethylbenzene (retention time ~ 22.8 min), the total area of the chromatogram from retention time of 5.4 minutes to 37 minutes was incorporated into the mass calculations. The "extended GRO" calculations were proportionally similar to the EPA defined GRO results for the Start and Final timepoints (Figure 16); however, the variations in the measurements were greater in the "extended GRO" analysis.

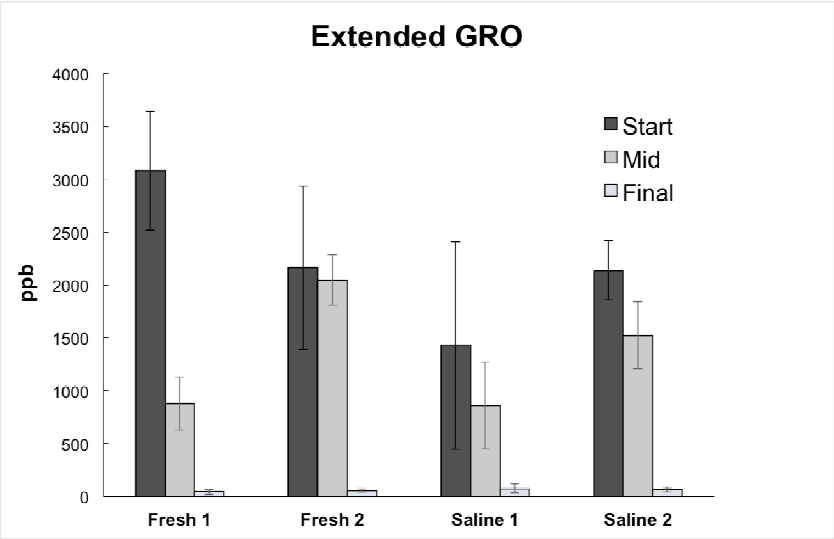

Figure 16: "Extended" gasoline range organic compound range, calculated by integrating the peak area between 2-methylpentane and the end of the GC run. The freshwater samples contain no salt and the saline samples contain 10,000 mg L^{-1} NaCl. Start = 18.5 h, Mid = 49 h, Final = 270 h.

A possible explanation for increased variability could be the behavior of surfactants in the frack fluid during the purge phase of the automated compound concentration step. Complete washing of the glass sparger between replicate analyses is difficult to achieve where the sample aliquot foamed and could cause carry-over. An "extended GRO" analysis is therefore unreliable to effectively quantify a broad hydrocarbon range in synthetic frack fluid, and higher boiling point compounds should be analyzed with organic extraction sample preparation.

3.2.3 Diesel Range Organic Compounds

The TDS concentrations in the low salinity samples affected the diesel range organic compound degradation. Freshwater samples had a mean degradation of 92 ± 0.7 %, while the 10,000 mg L^{-1} TDS samples had only 69 ± 1% degradation (Figure 17). The starting DRO concentrations were far greater in the Fresh samples than the Mid samples and can be attributed to the saline conditions as explained in Section 3.2.4. Percent reduction is less useful for this particular DRO analysis because each of the four samples had nearly the same final concentrations, perhaps reflecting a constant amount of recalcitrant material or organic degradation byproducts between the four samples.

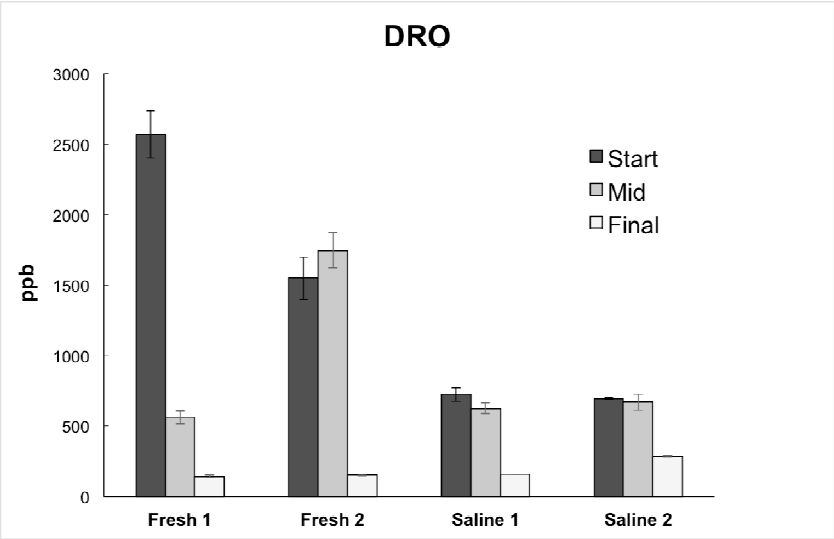

Figure 17: Diesel range organic compound degradation in synthetic frack fluid after three time points when spiked with 25 mg L^{-1} activated sludge. The freshwater samples contain no salt and the saline samples contain 10,000 mg L^{-1} NaCl. Start = 18.5 h, Mid = 49 h, Final = 270 h.

Again, the abiotic controls could not be analyzed because of the analytical challenges that the raw synthetic frack fluid presented. During the LLE sample preparation, a thick emulsion appeared after the first addition of solvent. EPA method 3510C for Separatory Funnel Liquid-Liquid Extraction calls for vigorous shaking of the funnel after the solvent addition; however, excessive mixing can create an emulsion due to the presence of polar surfactants in the aqueous solution [56]. A common remedy for this problem is a salting out technique by the addition of NaCl or an ion-pairing agent. Adding NaCl to the funnel did not

help salt out the emulsion into the organic phase, and the addition of an ion-pairing agent would have introduced a positive bias into the cumulative diesel range organics measurement. Further investigation into the AI600 corrosion inhibitor and Revert Flow stimulation surfactant ingredients of the synthetic frack fluid indicate the presence of ethoxylated nonylphenol and ethoxylated C_6-C_{12} alcohols, both of which do not partition well into an organic solvent during LLE. An extraction efficiency experiment was performed to quantify the extent of semi-volatile organic compound recovery with this laboratory method and is outlined in Appendix B. Future experiments will be designed to incorporate ion-exchange solid phase extraction into the sample preparation step or liquid-chromatography pair with mass spectrometry detection for polar organic compound analysis. These analytical difficulties might explain the anomaly between the "start" and "mid" time points of one of the freshwater replicates (Fresh 2; Figure 17).

The entire UCM in the chromatogram was incorporated into the DRO analysis, which allowed for a measure of quantitative reduction of the distillates and synthetic additives as a whole (Figure 18).

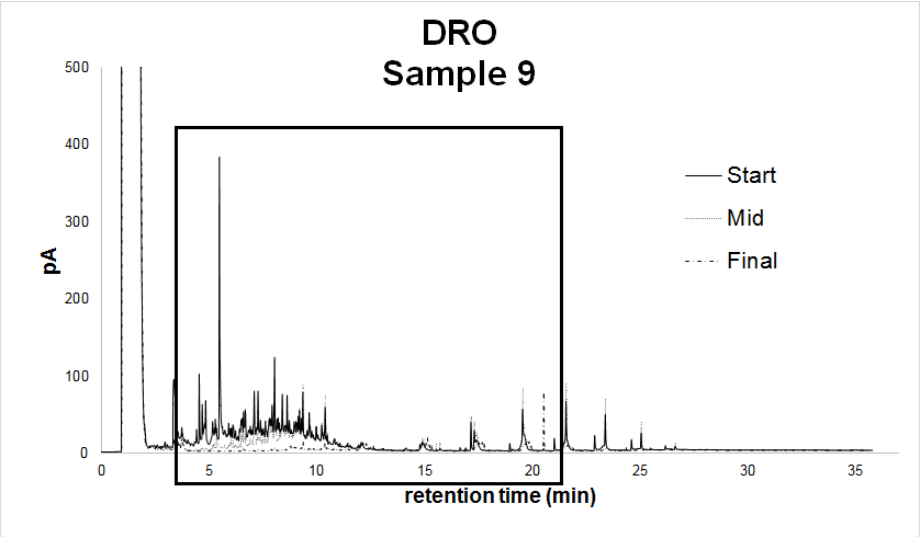

Figure 18: Chromatogram of a freshwater sample analyzed by GC-FID for DRO. The black box indicates the retention time range for DRO (C_{10} to C_{28}). Note the UCM and the extent to which it is incorporated into the DRO analysis.

DRO concentrations are therefore greater than the respective GRO concentrations because of the UCM quantification.

The mean final concentration of both the Freshwater samples and Mid salinity samples were 146 ± 8.1 ppb and 220 ± 4.5 ppb, respectively, indicating that salinity does not greatly affect the final concentrations after microbial degradation (Figure 16). The remaining DRO compounds in each sample after 270 hours need to be identified in future studies, as they are recalcitrant to biodegradation or are degradation byproducts. Targeted analysis of individual

compounds was not possible due to poor chromatographic resolution. Future analysis via higher resolution analytical instruments, such as GCxGC coupled with time-of-flight (TOF) mass spectrometry, would provide better insight into the individual compounds present in solution.

3.2.4 Loss from Salinity

Of the 54 targeted volatile organic compounds (Appendix A), one chemical was detected in all samples after each time point. A substituted benzene, 1,2,4-trichlorobenzene (1,2,4-TCB), remained in solution after 270 hours in the flasks and was deemed the most recalcitrant targeted compound in the experiment (Figure 19).

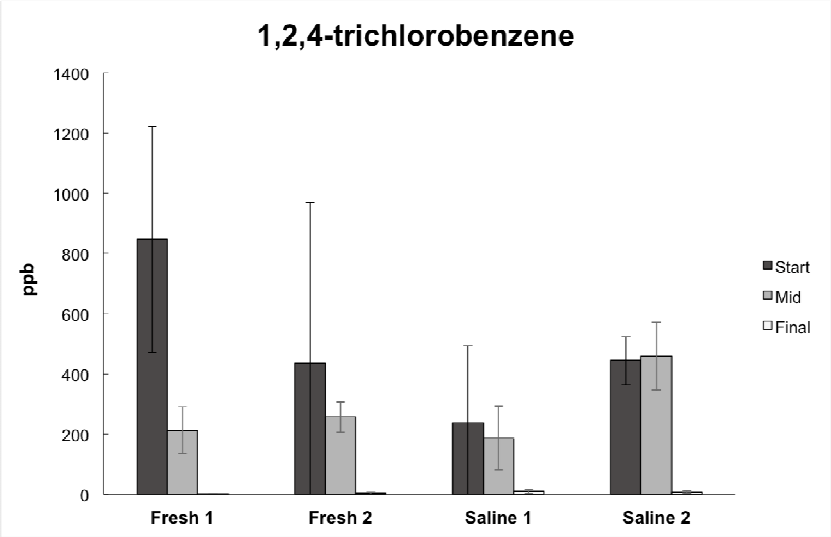

Figure 19: Concentration of 1,2,4-TCB after three time points when spiked with 25 mg L^{-1} activated sludge. The freshwater samples contain no salt and the saline samples contain 10,000 mg L^{-1} NaCl.

The compound 1,2,4-TCB exhibits similar trends across the four samples as GRO and DRO and therefore was used as a representative compound for a mass balance to better understand unexpected compound losses. The Freshwater synthetic frack fluid generally had greater starting concentrations of 1,2,4-TCB than the saline frack fluid, as did GRO and DRO. Two possible explanations for this result relate to the nature of organic chemicals in saline solutions: (1) salinity's effect on solubility and (2) sorptive losses to organic matter.

First, dissolved inorganic salts affect the solubility of organic compounds in solution [57]. The Setschenow constant relates the aqueous solubility of a chemical with the molar concentration of a salt to empirically predict the chemical's solubility in the saline solution according to Equation 3.

$$C_{salt} = C_w \cdot 10^{-k^s[salt]_{tot}} \quad \text{Eq. 3}$$

The Setschenow constant, k^s, is experimentally calculated and from published literature was found to be 0.25 M^{-1} for 1,2,4-TCB [58]. In a 10,000 mg L^{-1} NaCl solution with a known aqueous solubility of 1.659 x 10^{-4} M [57], the estimated solubility of 1,2,4-TCB is 6.201 x 10^{-5} M. The Henry's Law constant also changes with salinity and can be calculated by Equation 4 [59].

$$K_{h\,salt} = K_h \cdot 10^{k^s[salt]_{tot}} \quad \text{Eq. 4}$$

The K_h of 1,2,4-TCB in water is 0.093 [57] and is calculated to be 0.103 in a 10,000 mg L^{-1} NaCl solution. This 9.4% increase in K_h would account for some of the loss of 1,2,4-TCB recorded in the freshwater and saline solutions due to volatilization; however, the actual mean differences in GRO are close to 53% (Figure 18). Thus, salt-induced differences in partitioning behavior are not sufficient to explain the

observed differences in starting compound concentrations between freshwater and saline samples.

A second possible explanation for the discrepancy is that the activated sludge seed added to the flasks could act as a sink for organic compounds due to sorption. Sorption of neutral organic compounds to particulate organic matter (POM) increases as solution salinity increases [60, 61]. This phenomenon is explained not only by the salting out effect of the compound in a saline solution, but also by the increase in hydrophobicity of the POM. Means (1995) suggested that the polar functional characteristics of POM are neutralized, making it a better sorbent for hydrophobic organic compounds [62]. Incorporating the sorption of organic compounds to the activated sludge in a mass balance will provide a better understanding of the rate and extent of compound biodegradability. Such an estimate cannot be made currently because the partitioning coefficient of activated sludge is unknown.

Although analysis of abiotic controls would help assess the magnitude of the losses, we were unable to analyze them via Purge and Trap GC or prep them via LLE. Future experiments will employ compound fractionation techniques during sample preparation to reduce interferences in the analyses. Experiments

will also account for the loss of organic compounds in the synthetic frack fluid to POM by quantifying the fraction of organic carbon in activated sludge and various sediments and soils from areas where fracking fluid and wastes may be spilled. Sorption isotherm experiments on the sludge and soils will further our understanding of the organic compound losses and help us to better quantify the mass balance.

3.4 Conclusions and Future Research

These results provide a first assessment of the variability of natural attenuation potential across relevant salinity gradients. They also suggest that the majority of compounds used in frack fluid are inherently degradable under optimized conditions, but unknown recalcitrant compounds remain. Bulk dissolved organic carbon decreased 76 ± 2% in a freshwater solution of synthetic frack fluid over the course of 270 hours, and a 10,000 mg L^{-1} NaCl solution of the fluid recorded a 69 ±2% reduction. Observed DOC degradation of the higher salinity, 60,000 mg L^{-1} NaCl frack solution was minimal and the salinity proved to inhibit microbial degradation of organic compounds. Clearly, organic compounds are present in solution that are resistant to biodegradation with activated sludge as a starting seed. Gasoline range organic compounds were

reduced over 99 ± 1% in these open reactor vessels, however higher molecular weight semi-volatile compounds in the diesel range persisted over the course of the experiment.

3.4.1 Future Research

Future research will aim to identify recalcitrant compounds with higher precision analytical instruments and streamlined sample cleanup techniques. Method development will incorporate in-line solid phase extraction and acid-base partition cleanup to GC units for subsequent analysis via mass spectroscopic or flame-ionization detection (Figure 20). Rapid quantitative analysis will save time and resources and allow for more time points to be analyzed during batch reactor experiments.

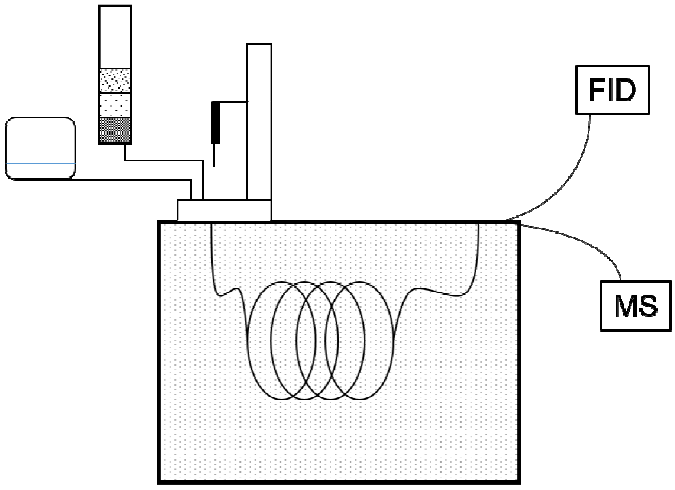

Figure 20: Streamlined method development for complex mixture analysis of hydraulic fracturing fluid and wastes including in-line solid phase extraction and acid-base partitioning sample cleanup.

Once identified, the recalcitrant compounds will be targeted for sorption experiments with varying soils, sediments, and POM. Future research will also investigate degradation rates and extents with specific microbes found in industrial wastewater treatment facilities, surface soils and sediments where spills can occur, and those found in extreme environments such as high temperature and high pressure geologic formations. Besides engineering and analytical applications, this research will also benefit the natural gas industry by determining the rate and extent of microbial degradation of the chemicals used for specific purposes in the extraction process downwell.

Appendix A:

Analytical Methods

Volatile Organic Compounds

Triplicate, 5-mL samples were analyzed via EPA Method 624 with minor modifications. Briefly, samples were pre-concentrated via purge and trap (Stratum PTC, Teledyne Techmar, Inc.; 4.0 min purge at 40 mL min^{-1}) and subsequently analyzed via gas chromatography – flame ionization detection (GC-FID; Agilent 7890A; DB-624 column; 60m x 320 µm x 1.8 µm; 6 mL min^{-1} carrier flow, 2.0 min hold at 40 °C, ramp 4 °C min^{-1} to 150 °C, then 8 °C min^{-1} to 200 °C). Detection limits were calculated as three times the signal of several HPLC grade water blanks (i.e., three times the noise). VOCs were quantified with a 54 compound external standard (502.2 MegaMix; Restek Corp.). To confirm compound identities, replicates were pre-concentrated and subsequently analyzed via GC-mass spectrometry (GC-MS; Agilent 7890A-5975C quadrupole MS detector; EI mode).

Gasoline Range Organic Compounds

Gasoline range organic compounds were analyzed following EPA Method 8015D for non-halogenated organics using GC-FID alongside VOC analysis. GRO

was calculated as the total area of all peaks above the detection limit between 3-methylpentane and 1,2,4-trimethylbenzene (using external standard GRO # 30065; Restek Corp.) for all samples.

Diesel Range Organic Compounds

Liquid-liquid extractions were performed to prepare the samples for diesel range organic compound analysis. A known volume of sample was added to a 500-mL separatory funnel along with approximately 50 mL of dichloromethane (DCM) and methanol (MeOH) (90:10). The funnels were shaken vigorously and allowed to sit for at least 15 minutes to equilibrate before collecting the organic phase in a round bottom flask. This process was repeated three times and the aqueous phase was then discarded. A small amount (~20 mg) anhydrous sodium sulfate was added to the round bottom flasks as a drying agent and the organic phase was transferred to another flask for evaporation. The extracts were then evaporated with a rotary evaporator to approximately 1 mL. The remaining extracts were filtered through precombusted silica-gel filters that had been conditioned with 10 mL DCM:MeOH (90:10), and then rinsed with 20 mL DCM:MeOH. The final extracts were rotary evaporated to 1 mL and transferred to 2-mL autosampler vials.

Diesel range organic compound analysis followed EPA Method 8015D for non-halogenated organics using GC-FID. A G4513A autosampler (Agilent Technologies, Inc.) with a 10-µL gastight syringe was used to inject the non-aqueous sample onto the 7890A gas chromatography system. The gastight syringe was washed three times with hexanes and dichloromethane before and after each injection. A 5%-phenyl-methylpolysiloxane column (HP-5, Agilent Technologies, Inc.) was installed for the DRO analysis (30 m x 0.320 mm x 0.25 um, 2 mL/min flow, 9.14 psi, 0 minute hold at 40ºC, ramp to 300ºC at 10ºC/min). The FID was programmed to 250ºC, 30 mL/min H_2 flow, 400 mL/min air flow, signal data rate at 20 Hz and minimum peak width 0.01 minutes (0.6 s).

Total diesel range organic compound concentrations in each sample were calculated by integrating the total peak areas between the retention times for C_{10} and C_{28} and dividing by the response factor of a five point external DRO standard mix (DRO #31064, Restek Corp.). Detection limits were calculated as three times the signal of several dichloromethane blanks.

Appendix B

Extraction Efficiency

An isotopically labeled surrogate and injection standard was used to calculate LLE efficiency and instrument injection efficiency, respectively. Groundwater was used to represent a matrix similar to the actual samples collected in the field for the groundwater organic geochemistry characterization experiments. The extraction procedure used to analyze for DRO compounds was replicated, however, 100 µL of 0.05 ng μL^{-1} deuterated PAH-SIM Recovery Standard Mixture (ES-5386, Cambridge Isotope Laboratories, Inc.) was added prior to the first round of shaking and equilibration. Following the final rotary evaporation, 900 µL of the extract was added to an amber GC vial along with 100 µL of 0.05 ng μL^{-1} deuterated PAH Mix (ES-5481, Cambridge Isotope Laboratories, Inc.). A control vial containing 100 µL of 0.05 ng μL^{-1} recovery and injection standard was added to the analysis sequence. The sample vials were then analyzed on the 7890A/5979C GC-MS system with a G4513 autosampler (Agilent Technologies, Inc.).

Injection standard mass was calculated using Equation 6 for each of the six deuterated compounds in the PAH Mix.

$$M_{IS} = \frac{A_{ISS} * M_{ADD}}{A_{ISC} * RF_{ISC}} \quad \text{Eq. 6}$$

where:

M_{IS} = calculated injection standard mass

A_{ISS} = integrated area of injection standard added to a sample

M_{ADD} = known mass of injection standard added to each sample

A_{ISC} = integrated area of injection standard from control vial

RF_{ISC} = injection standard response factor of the control vial

Recovery standard mass was calculated with Equation 7 for each of the four deuterated compounds in the PAH-SIM recovery standard mixture.

$$M_{RS} = \frac{A_{ISS} * M_{CALC}}{A_{ISS} * RF_{RSC}} \quad \text{Eq. 7}$$

where:

M_{RS} = integrated area of recovery standard added to each sample

M_{CALC} = calculated mass of injection standard

A_{ISS} = area of injection standard compound added to each sample

RF_{RSC} = recovery standard response factor of the control vial

The injection standard compound to elute immediately following the calculated recovery standard compound was used in Equation 7. For example, the recovered mass of injection compound acenaphthene-d_{10} (retention time 10.321 minutes) was referenced as *MI* to calculate the mass of recovery compound 2-methylnaphthalene-d_{10} (retention time 7.835 minutes) because it was the next injection standard compound to elute.

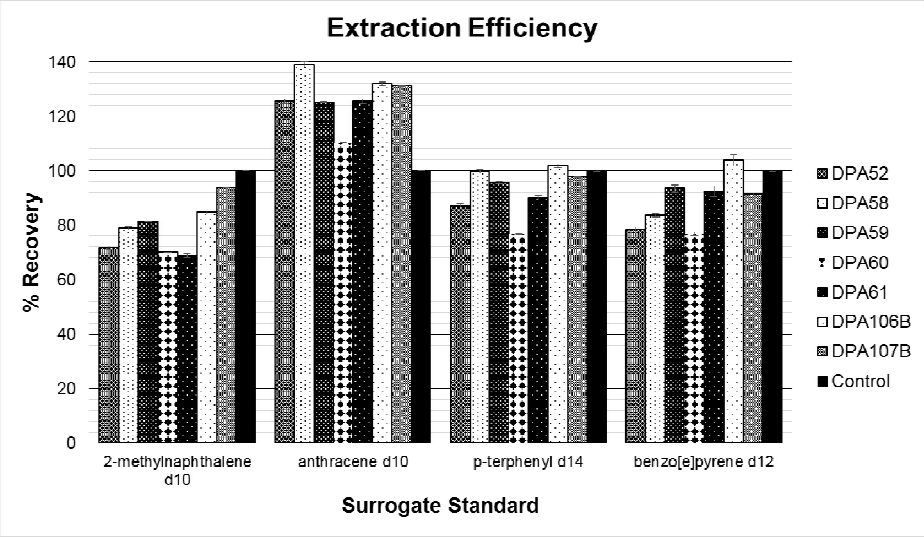

Figure 21: Liquid-liquid extraction percent recoveries of four isotopically labeled surrogate standards in groundwater.

This method to evaluate liquid-liquid extraction efficiency provided detailed results of the laboratory technique used to extract DRO compounds from aqueous solutions. Four deuterated polycyclic aromatic hydrocarbons (PAH) from 152 – 264 Da were successfully recovered with good precision in seven groundwater samples (Figure 19). Percent recovery ranged from 68% (2-methylnaphthalene-d_{10}) to 138% (anthracene-d_{10}). Naphthalene is a notoriously difficult semi-volatile compound to recover from aqueous solutions with liquid-liquid extraction and rotary evaporation. 2-methylnaphthalene has a slightly higher boiling point (241 ºC compared to 218 ºC) and theoretically would produce better recovery than naphthalene, therefore recovery for low boiling point semi-volatile compounds are estimated to be around 65 – 80%. Future semi-volatile organic compound analysis will include more equilibration time in the separatory funnel, as the EPA recommended minimum of 10 minutes may be inadequate for high recovery with this laboratory method [56].

Appendix C

Detection Limits

Table 4: Detection limits for DRO, GRO, and individual VOCs.

Compound	LOD (ppb)	Compound	LOD (ppb)
DRO	0.090	1,2-Dibromoethane	0.172
GRO	0.026	Chlorobenzene	1.816
1,1-Dichloroethene	0.840	Ethylbenzene	2.853
Methylene chloride	1.018	m-Xylene+p-xylene	4.984
1,1-Dichloroethane	0.471	o-Xylene	2.375
trans-1,2-Dichloroethene	1.224	Styrene	0.258
2,2-Dichloropropane	2.363	Bromoform	8.961
cis-1,2-Dichloroethene	2.363	1,2,3-Trichloropropane	0.321
Chloroform	2.723	Bromobenzene	0.539
Bromochloromethane	1.465	1,1,2,2-Tetrachloroethane	1.237
Carbon tetrachloride	0.830	n-Proplbnezene	0.342
1,1,1-Trichloroethane	0.830	2-Chlorotoluene	0.393
1,1-Dichloropropene	0.830	1,3,5-Trimethylbenzene	0.186
Benzene	0.197	tert-Butylbenzene	0.368
1,2-Dichloroethane	0.529	1,2,4-Trimethylbenzene	0.347
Trichloroethene	1.247	sec-Butylbenzene	0.422
1,2-Dichloropropane	0.696	1,3-Dichlorobenzene	0.554
Bromodichloromethane	4.169	1,4-Dichlorobenzene	0.239
Dibromomethane	4.080	4-Isopropyltoluene	0.239
cis-1,3-Dichloropropene	0.906	1,2-Dichlorobenzene	0.562
Toluene	0.256	n-Butylbenzene	0.494
trans-1,3-Dichloropropene	1.217	1,2-Dibromo-3-Chloropropane	7.222
1,1,2-Trichloroethane	1.505	1,2,4-Trichlorobenzene	1.013
Tetrachloroethene	0.413	Hexachlorobuatdiene	2.585
1,3-Dichloropropane	0.660	Napthalene	0.875
Dibromochloromethane	0.099	1,2,3-Trichlorobenzene	1.092

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